

THE INTERACTION OF LOW ENERGY ELECTRONS WITH POLYMERIC PERFLUORINATED ETHYLENEPROPYLENE (FEP)(1)

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ABSTRACT: Photomicrographs are presented showing the effects of 30 Kev electrons on FEP. Depicted are Lichtenberg patterns, bubbles and a buckling effect. The attempt to explain these observations is derived from a theoretical analysis based on a diffusion mechanism for charge flow using beam current as a source term. The solution is used to demonstrate that charge is stored centrosymmetrically with respect to ground. These effects are discussed in terms of an "electrolysis" mechanism resulting from charge storage and beam energy thermalization. Explicit expressions are given for surface charge storage and voltage across the sample resulting from such charge accumulation. Buckling is treated from a thermodynamic basis using the Helmholtz free energy and assuming the distortion develops isothermally. "Electrolysis" is postulated via a mechanism selecting the tertiary carbon as the active site for mobile moiety generation.

The usefullness of optical data for purposes of thermal design taken from samples irradiated with low energy electrons in the laboratory is questioned. Because FEP is an electrical insulator, these experiments must, therefore, be carried out in a neutral laboratory environment, or be characterized in the space environment from carefully designed electrical experiments.

KEY WORDS: degradation mechanising, electron bombardment, electron degredation, polymeric perfluorinated ethylenepropylene proton bombardment, thermal control coatings

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Introduction

Few spacecraft thermal control materials have received as much undocumented attention as perfluorinated polyethylenepropylene (FEP). This unusual ascendency of FEP into prominence occurred because encouraging thermal information obtained from flight data^(2,3) were available prior to laboratory tests qualified from optical measurements.

That the performance of metallized FEP as a second surface mirror appreciably surpasses white paints cannot be doubted; (4) yet, its qualification in the laboratory cannot be judged as altogether routine. For example, irradiating with ultraviolet photons or 2 - 30 Kev protons gives reproducible data under carefully controlled conditions, whereas irradiations carried out with electrons characterized similarly to their proton counterpart will not give a degradation sufficiently uniform for optical measurement. This treatment provides an elucidation of this "unconventional" behavior of FEP toward electrons.

In the following section, experimental observations of electron irradiated FEP are presented and discussed with the detailed objective of providing a basis for a theoretical development of the charge storage function c(r,z,t). Subsequently, the stability problem is discussed in a heuristic manner using some notions of control theory and simple electric circuits. A brief thermodynamic description is presented and a solution to the complete problem is outlined accounting for chemical reactions or "electrolysis" of the film. Finally, recommendations are put forth regarding electron stability testing of electric insulators.

Experimental Observations

Perfluorinated polyehtylenepropylene copolymer units comprise the FEP⁽⁵⁾ network in a manner yielding a material susceptible to sublimation. That FEP is indeed subject to vaporization, resulting from thermalization of a 30 Kev proton beam, is shown in Figure 1. The area surrounding the puncture contains proton beam generated charge rearrangements detectable by optical means as additional ultraviolet absorption sites having the usual long wavelength cutoff extending deep enough into the visible portion of the spectrum to create a brown color. The puncture occurred near the center of unmetallized material or at the point furthest from ground. The experiment was

^(2,3,4,5) The numbers in parentheses refer to the list of references appended to this paper.

repeated using a grid placed about 30 mils above silver coated 5 mil FEP. Experiments were performed with both grid and sample holder at ground potential and with the grid at +300 volts above ground. Results were similar and reproducible for both cases. Figure 2 shows the configuration. Figure 3 is a photograph of the area comprising one section of the grid.

Although not clearly shown in Figure 3, the mesh centered portions of the FEP generate ultraviolet centered optical changes possessing absorption tails extending far enough into the visible portion of the spectrum to show the familiar brown color. Again, heating appeared to take place in portions furthest below ground electrically. Clearly visible are dentrite-like Lichtenberg patterns⁽⁶⁾ emanating from the center of the sample and extending toward portions shadowed from the electron beam by the grid. Figure 4 reveals the existence of these dentritic patterns amid clusters of bubbles. It appears likely therefore that charge is stored at least in the neighborhood of the surface of the material, preferably at its geometric center relative to the mesh. Referring again to Figure 3, it is apparent that the surface of the sample is not in relative focus owing to the buckled central region where charge storage and thermalization occur. Figure 5 shows this effect schematically. Notice that the metallic film maintained its adhesion to the FEP.

In summary then, it appears reasonable to assume that 5 mil FEP whether metallized or not can at least store charge in the neighborhood of its surface and in a region furthest from ground. The conversion of beam kinetic energy into thermal energy in the presence of stored charge gives rise to an "electrolysis" or bubbling of the material and, therefore, the formation of dentrites capable of carrying charge to ground; ground itself being made more accessible via the grid by means of a buckling mechanism. Figure 6 depicts the veined network common to virtually all beam shadowed areas where charge also arcs to ground. It is the charge storage problem and its relationship to the grounding of the sample that forms the basis for the following section.

The Charge Storage Problem

The phenomenology of electron storage in electrical insulators and dielectrics can be treated in a manner formally identical to a

⁽⁶⁾ The numbers in parentheses refer to the list of references appended to this paper.

corresponding thermal problem. Our starting point is, therefore, the diffusion equation:

$$\frac{\partial c(r,z,t)}{\partial t} = D\nabla^2 c(r,z,t) + \nabla F(z)$$
 (1)

where:

c(r, z, t) = number of charges at the point (r, z, t),

t = time,

D = a diffusion constant and,

(r, z) = an arbitrary point in cylindrical space.

Because we take for simplicity that charge is incident normal to the surface at z=0, the angular dependency is automatically eliminated from the equation. The function F(z) or source term is the solution of

$$-\frac{\mathrm{d}\mathbf{F}(\mathbf{z})}{\mathrm{d}\mathbf{z}} = k\mathbf{N}_0\mathbf{F}(\mathbf{z}), \qquad (2)$$

the usual penetration equation governing spatial dependencies norma to the incident particles. The parameter k represents a number characterizing the capture cross-section of the storage site, while N_0 is the site density. Solving (2) and substituting into (1) gives

$$\frac{\partial c}{\partial t} = D\nabla^2 c - N_0 k F_0 e^{-kN_0 z} = D\nabla^2 c - f(z)$$
 (3)

where F_0 is proportional incident particle momentum. We obtain the solution of (3) as the sum of two functions, (7)

$$c(r, z, t) = u(r, z) + w(r, z, t),$$
 (4)

with w = 0 when z = 0. It follows that

$$\frac{\partial^2 \mathbf{u}}{\partial \mathbf{r}^2} + \frac{\mathbf{1}}{\mathbf{r}} \frac{\partial \mathbf{u}}{\partial \mathbf{r}} + \frac{\partial^2 \mathbf{u}}{\partial \mathbf{z}^2} - \frac{\mathbf{f}(\mathbf{z})}{\mathbf{D}} = 0$$
 (5)

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and

$$\frac{1 \partial w}{D \partial t} = \frac{\partial^2 w}{\partial r^2} + \frac{1 \partial w}{r \partial r} + \frac{\partial^2 w}{\partial z^2}$$
 (6)

A solution to (5) is sought in the form

$$u = \sum_{i} \phi_{i}(r) \psi_{i}(z)$$
 (7)

with ϕ_{i} (r) forming an orthonormal set. Substitution of (7) into (5) shows that the ϕ_{i} 's are Bessel functions of zero order with ψ_{i} being a solution of

$$\frac{\partial^{2} \psi_{i}}{\partial z^{2}} - \left(\frac{\alpha_{i}}{R}\right)^{2} \psi_{i} = \frac{1}{\alpha_{i}} \frac{J_{1}(\alpha_{i})}{D} \frac{2 f(z)}{J_{0}^{2}(\alpha_{i}) + J_{1}^{2}(\alpha_{i})} = g(z)$$
 (8)

where α_i is a zero of $J_0(\mu R)$, since the sample is assumed at ground potential for r=R. The parameter μ is a separation constant. $Y_0(\mu r)$ was eliminated as a solution, since c(0,z,t) must be finite. The Greens function solution of (8) was obtained using the usual symmetric boundary conditions,

$$G_{<}(0) = 0 \text{ and } G_{>}(d) = 0,$$
 (9)

where d is the thickness of the sample. The result is

$$G = \theta(\xi - z) \frac{\sin h\mu(d - \xi)}{\mu \sin h\mu d} \sin h\mu z + \theta(z - \xi) \frac{\sin h\mu \xi}{\mu \sin h\mu d} \sin h\mu(d - z)$$
(10)
$$= G_{<}(\xi, z) + G_{>}(z, \xi),$$

with θ representing the Heaviside step function. The particular solution to (8) is then given by

$$\psi_{\mathbf{P}}(z) = \int_{0}^{z} G_{<}(\xi, z) g(\xi) d\xi + \int_{z}^{d} G_{>}(z, \xi) g(\xi) d\xi$$

$$= \frac{M \sin h \mu z}{2 \mu \sin h \mu d} \left[\frac{e^{\mu d}}{(\mu + k N_0)} \left(1 - e^{-(\mu + k N_0)z} \right) + \frac{e^{\mu d}}{(k N_0 - \mu)} \right]$$

$$\left(1 - e^{-(kN_0 - \mu)z}\right] + \frac{M \sin h\mu (d-z)}{2\mu \sin h\mu d} \left[\frac{1}{(kN_0 - \mu)}\right] e^{-(kN_0 - \mu)z} - e^{-(kN_0 - \mu)d}$$

+
$$\frac{1}{(\mu + kN_0)} \left(e^{-(\mu + kN_0)z} - e^{-(\mu + kN_0)d} \right]$$
 (11)

where

$$M = \frac{1}{\alpha_i} \frac{J_1(\alpha_i)}{D} \frac{2F_0 N_0 k}{J_0^2(\alpha_i) + J_1^2(\alpha_i)}$$

The homogeneous solution is of the form

$$\psi_{\mathbf{u}} = \overline{\mathbf{A}} e^{\mu z} + \overline{\mathbf{B}} e^{-\mu z}$$

with the total solution written as

$$\psi_{\mathbf{T}} = \psi_{\mathbf{H}} + \psi_{\mathbf{P}} \tag{12}$$

 \mathbf{or}

$$\psi_{\mathbf{T}} = \sum_{i} \frac{2}{\alpha_{i}} \frac{J_{1}(\alpha_{i})}{J_{0}^{2}(\alpha_{i}) + J_{1}^{2}(\alpha_{i})} \frac{F_{0}}{DkN_{0}} \left[1 + \frac{e^{-\mu d}}{\sinh \mu d} \sinh \mu z\right] + \psi_{\mathbf{P}}$$
(13)

where $\psi_{\mathbf{P}}$ is given by equation (11). The complete solution is now reduced to the form

$$\mathbf{c}(\mathbf{r}, \mathbf{z}, \mathbf{t}) = \sum_{i=1}^{n} \left(\psi_{\mathbf{H}_{i}} + \psi_{\mathbf{P}_{i}} \right) \phi_{i} + \mathbf{w}, \qquad (14)$$

where the solution for w remains to be determined.

If we choose

$$w(r, z, t) = w_1(r) w_2(z) w_3(t)$$
 (15)

then

$$w_1 = A_1 J_0(\mu r) + B_1 Y_0(\mu r)$$

and $B_1=0$ since w_1 must be finite for r=0 , and as before $J_0\left(\mu R\right)=0$ to satisfy our grounding condition. Therefore,

$$w_1 = A_1 J_0(\alpha_i x)$$

with 0 < x < 1 in place of 0 < r < R. Continuing the partitioning to obtain equations for $\rm w_2$ and $\rm w_3$, we obtain

$$\frac{\partial^2 w_2}{\partial z^2} + \lambda^2 w_2 = 0 \tag{16}$$

and

$$\frac{1}{\mathbf{w_3}\mathbf{D}} \frac{\partial \mathbf{w_3}}{\partial \mathbf{t}} = -\lambda^2 - \mu^2 \tag{17}$$

If we write

$$w_2 = A_2 \sin \lambda z + B_2 \cos \lambda z$$

and

$$w_3 = A_3 e^{-(\lambda^2 + \mu^2)Dt}$$

equation (15) becomes

$$w = \sum_{i} e^{-(\lambda^2 + \mu^2)Dt} J_0(\alpha_i r) \left[A_2^i \sin \lambda z + B_2^i \cos \lambda z \right]$$
 (18)

The constant B_2' is determined from the grounding requirement that w=0 when z=d for $0 \le x \le 1$ ($0 \le r \le R$) giving $B_2'=0$. The parameter λ is determined from the zeros of $\sin \lambda d$ or

$$\lambda = 2\pi n/d$$

and

$$w(r,z,t) = \sum_{i} A_{2} e^{-\left\{\left(\frac{2n\pi}{d}\right)^{2} + \left(\frac{\alpha_{i}}{R}\right)^{2}\right\}} J_{0}(\alpha_{i}k) \sin\left(2n\pi \frac{z}{d}\right) (19)$$

Thus far we have demonstrated that our charge storage solution can be put into the form

$$c(\mathbf{r}, \mathbf{z}, \mathbf{t}) = \sum_{i} \left\{ \left(\overline{\mathbf{A}}_{i} e^{\mu \mathbf{z}} + \overline{\mathbf{B}}_{i} e^{-\mu \mathbf{z}} \right) + \psi_{\mathbf{P}} J_{0}(\alpha_{i} \mathbf{k}) \right\}$$

$$+ \sum_{i} \sum_{i} \mathbf{A}_{n_{i}} e^{-\left\{ \left(\frac{2n\pi}{d} \right)^{2} + \left(\frac{\alpha_{i}}{R} \right)^{2} \right\} Dt} J_{0}(\alpha_{i} \psi) \sin \left(\frac{2n\pi \mathbf{z}}{d} \right)$$

$$(20)$$

To determine $\overline{\mathbf{A}}_{\mathbf{i}}$, $\overline{\mathbf{B}}_{\mathbf{i}}$, and \mathbf{A}_{2} we apply our grounding condition

$$c(r,d,t) = 0, 0 < r < R, 0 < t < \infty$$
 (21)

followed by the surface requirement

$$c(r, 0, t) = F_0/kN_0D, 0 < r < R, 0 < t < \infty$$
 (22)

and finally the initial condition that the sample carries no initial charge, or

$$c(r, z, 0) = 0.$$
 $0 < r < R, 0 < z < d$ (23)

Applying the boundary conditions (21), (22), and (23) in the order listed gives

$$\overline{A}_{i} = \frac{J_{1}(\alpha_{i})}{\alpha_{i}} \frac{\overline{F}_{0} e^{-\mu d}}{k N_{0} D \sin h \mu d} \frac{1}{\left\{J_{0}^{2}(\alpha_{i}) + J_{1}^{2}(\alpha_{i})\right\}}$$

$$B_i = -A_i e^{2\mu d}$$

and

$$A_{ni} = \frac{2F_0 J_1(\alpha_i)}{kN_0 D\alpha_i \left\{ J_0^2(\alpha_i) + J_1^2(\alpha_i) \right\}} \frac{1}{(2\pi n) \left\{ \frac{(\alpha_i)^2}{R} + \left(\frac{2\pi n}{d} \right)^2 \right\}}$$
(24)

with A_i being determined from a Fourier-Bessel's expansion and $A_{n\,i}$ from both Fourier and Fourier-Bessel's expansions.

Discussion of the Relationship Between Charge Storage and Stability

There exist two conduction paths for the escape of absorbed charge to ground: along the surface and through the bulk. Brief consideration determines that these routes can be represented most simply as two resistances connected in parallel. Let us write expressions for local resistances in the form

$$R_{\text{bulk}} = R_z = \frac{\rho(d-z)}{\pi r^2}$$
 and $R_{\text{surface}} = R_r = \frac{\rho(R-r)}{2\pi r z}$

where the locality is given by (r, z) for a sample of size (R, d) and ρ is the resistivity. Combining these expressions in parallel, the local equivalent resistance, R(r, z) becomes

$$R(r,z) = \frac{\rho}{\pi r} \frac{(d-z)(R-r)}{2z(d-z) + r(R-r)}$$
 (25)

Taking the limit for z we obtain

$$R(r,0) = R = \frac{\rho d}{\pi r^2},$$

while if in addition the limit for r approaching zero is taken,

$$R(0,0) = R(r,0) = \infty,$$

$$\lim_{r \to 0} r \to 0$$

a divergent expression results.⁽⁸⁾ In both cases the local resistance about the origin gives a divergent result, suggesting that the closer an electron is to the origin the more difficult its migration to ground becomes. Hence the conjecture that charge is stored in the center of the sample or farthest from ground appears to be a reasonable one. Using this approach, however, the divergence of R (0,0) cannot be removed; but, having anticipated this result the diffusion equation was solved in the previous section to remove this divergence. From equations (14) and (15), the storage function is most compactly written in the form

$$c(\mathbf{r}, \mathbf{z}, \mathbf{t}) = \sum_{i} \phi(\alpha_{i} \mathbf{x}) \left\{ \psi_{H}(\mathbf{z}) + \psi_{P}(\mathbf{z}) \right\} + \sum_{i} \sum_{p} \phi(\alpha_{i} \mathbf{x}) w_{2}(\mathbf{z}) w_{3}(\mathbf{t}),$$
(26)

where use has been made of the identity $\phi(\alpha_i x) = w_1(\alpha_i x)$. Our boundary condition on the radial solution to equation (15), demanding the convergence of c(r,z,t) at c(r,0,t) and c(0,0,t), eliminated the divergent Neumann function. Inspection of equation (11) for ψ_P , equation (13) for ψ_H , and the result $J_0(0) = 1$, gives an expression for the number of charges stored in the neighborhood of the origin:

$$c(0,0,t) = \sum_{i} \psi_{H}(\alpha_{i}) + \psi_{P}$$

⁽⁸⁾The numbers in parentheses refer to the list of references appended to this paper.

$$= \sum_{i} \frac{2}{\alpha_{i}} \left\{ \frac{J_{1}(\alpha_{i})}{J_{0}^{2}(\alpha_{i}) + J_{1}^{2}(\alpha_{i})} \frac{F_{0}}{DkN_{0}} + \frac{M}{2\mu} \left[\frac{1}{(kN_{0} - \mu)} \left(1 - e^{-(kN_{0} - \mu)d}\right) + \frac{1}{(kN_{0} + \mu)} \left(1 - e^{-(kN_{0} + \mu)d}\right) \right]$$
(27)

with M being given in equation (11).

By inspecting the above result the generalized surface charge storage expression is obtained:

$$c(r,0,t) = \sum_{i} c(0,0,t) J_0(\alpha_i x).$$
 (28)

Equation (26) shows that the charge stored at (0,0) is indeed finite and that

$$\overline{F} R(r,0) = e c(r,0) C$$
 (29)

where

e = electronic charge,

C = surface capacitance at (r, 0), and

 \overline{F} = electron current.

Equations (27) and (28) show that $\overline{F}R(0,0) = V(0,0)$ is finite.

However, $R \sim \rho = 1/\sigma$

where σ is the conductivity. Writing

$$\sigma = c(0,0,t) e \mu_e$$

where e and $\mu_{\rm e}$ represent electronic charge and mobility, respectively, we can conclude that R(0,0) is finite. Next we wish to calculate the number charges stored on the surface of the sample. The result is obtained by integrating c(r, 0, t) over the surface of the sample:

$$c_s = \sum_i \int c(0,0,t) J_0(a_i x) r dr d\theta$$

$$= 2\pi R^2 c(0,0,t) \sum_{i} \frac{J_1(\alpha_i)}{\alpha_i}$$
 (30)

The number of charges per unit area is then given by

$$e_{s} = \frac{c_{s}}{\pi R^{2}} = 2 c(0,0,t) \sum_{i} \frac{J_{1}(\alpha_{i})}{\alpha_{i}}$$
 (31)

Since the voltage supported by a capacitor is given by definition as

$$V = qC, (32)$$

where q and C are charge and capacitance, respectively, we automatically have an expression for the voltage across any undamaged sample,

$$V = ec_s C, (33)$$

a quantity subject to calculation and measurement.

At the on set of this section, we discussed the conduction paths as a parallel arrangement of resistances, purposefully neglecting their respective path capacitances. It is clear from the photographs discussed in the first section, that material instabilities can be generated under quite moderate irradiation conditions. Further, it has been suggested that thermalization and charge storage cooperatively induce material changes. In a heuristic manner, then, we suggest that the initial charge storage sites become inductively altered once saturation has been reached, and propose a black box scheme to model the course of events. Shown in Figure 7 is a simple feedback loop represented by the transfer function Y_2 (p) or a time delayed degradation mechanism serving to modify the voltage generated across the circuit with transfer function Y_1 (p), the initial charge storage mechanism. The circuit transfer function Y_0 (p) is given by

$$Y_0(p) = \frac{V_0}{V_s} = \frac{Y_1(p)}{1 - Y_1(p) Y_2(p)},$$
 (34)

where the stability conditions are related to the voltage discharge frequency (p) to ground via the grid. It follows that stability will be determined by the zeros and poles of the function

$$Y_1(p) Y_2(p) - 1 = 0$$

The transfer functions are accordingly generated from the circuit analogy selected to represent the physical situation. This aspect of the problem will not be carried further here, but rather reserved for a future publication.

Before concluding this section, by reviewing the problem from a mechanisms point of view, the buckling phenomenon will be briefly discussed using a thermodynamic approach. As a starting point we assume that the occurrence of buckling could take place isothermally, that is,

$$\left(\frac{\partial \mathbf{F}}{\partial \nu}\right)_{\mathbf{T}} = -\mathbf{p}_{\mathbf{v}} + \mu \left.\frac{\partial \mathbf{c}(\mathbf{r}, \mathbf{z}, \infty)}{\partial \nu}\right|_{\mathbf{T}} + \frac{1}{2} \epsilon \left(\frac{\mathbf{V}}{\mathbf{d}}\right)^{2} \tag{35}$$

where

F = Helmholtz free energy,

p, = vapor pressure of the FEP,

 μ = chemical potential,

 $c(r,z,\infty) = terminal number of stored charges (t = \infty),$

 ν = volume, and

 ϵ = dielectric constant.

Next we make the substitution for the dielectric constant

$$\epsilon = 1 + 4\pi P \frac{d}{V}$$
 (36)

and take

$$\left(\frac{\partial \mathbf{F}}{\partial \mathbf{F}}\right)_{\mathbf{T}} = \mathbf{0}$$

to obtain

$$p_{v} = \mu \frac{\partial c(r, z, \infty)}{\partial v} \bigg|_{T} + \frac{1}{2} \bigg(\bigg(\frac{V}{d} \bigg)^{2} + 4\pi P \frac{V}{d} \bigg), \qquad (37)$$

where P is the polarization. Equation (37) expresses the charge buckling effect in terms of the vapor pressure p_{ν} , of the expanded surface. To rewrite the equation in terms of the vapor pressure p_{ω} of the undeformed material and the surface energy, use is made of the relationship between surface pressure and curvature:

$$p_{v} = p_{\infty} - \frac{\gamma}{R_{1}} - \frac{\gamma}{R_{2}}$$
 (38)

where γ is the surface energy and ${\rm R}_1$ and ${\rm R}_2$ the principal radii of curvature. Our final result is

$$\mu \left. \frac{\partial c(\mathbf{r}, \mathbf{z}, \infty)}{\partial \nu} \right|_{\mathbf{r}} = \mathbf{p}_{\infty} - \gamma \left\{ \frac{1}{R_1} + \frac{1}{R_2} \right\} + \left(\frac{\mathbf{V}}{\mathbf{d}} \right)^2 + 2\pi \mathbf{P} \frac{\mathbf{V}}{\mathbf{d}}$$
(39)

If FEP is "electrolyzed" under the influence of an electron beam and an expansion or buckling results, the surface curvature effect enters in a way such that the vapor pressure of the material will tend to be maintained at its original level. To simplify the argument we take $p_{\infty}\,=\,0$ and $R_{\,1}\,=\,R_{\,2}$ or

$$\mu \frac{\partial \mathbf{c}}{\partial \nu} \bigg|_{\mathbf{T}} = -\frac{2\gamma}{R_1} + \left(\frac{\mathbf{V}}{\mathbf{d}}\right)^2 + 2\pi \mathbf{P} \frac{\mathbf{V}}{\mathbf{d}}$$
 (40)

when

$$\frac{2\gamma}{R_1} > 2\pi \frac{PV}{d} + \left(\frac{V}{d}\right)^2$$

Then $\mu \left. \frac{\partial \, c}{\partial \, \nu} \right|_T < 0$, and the tendency toward volume charge storage is diminished and γ becomes a factor in the behavior. On expansion d will increase allowing for some increase in P and V if field strength is maintained. The relationship of the surface effect to bulk storage suggests buckling and charge escape to the grid is manifested by an "electrolysis" effect. We are now prepared to relate the stability problem to the chemical nature of FEP. Quite generally we can write the copolymer in the form

$$\begin{array}{c|c}
C F_3 \\
 & C \\
C F_2 - C F_2 - C \\
 & F
\end{array}$$
(41)

assuming the ethylene and propylene units are combined in equimolar amounts. If FEP stores appreciable charge prior to damage, then a small degree of unsaturation may be present. Next the tertiary carbon becomes suspect as a source of charge imbalance by virtue of the known stability of the carbanion. We are led to assume

and similarly for extraction of the fluoride moiety. A "crystallization" or cross linking reaction can be written for tertiary radicals,

$$2 - \dot{C}^{(\cdot -)} \longrightarrow - \dot{C} - \dot{C} \longrightarrow + (2e)$$

$$(44)$$

with the products $CF_3^{(-)}$ and $F^{(-)}$ becoming suitable candidates for transporting charge to the grid⁽⁹⁾, where discharge or the "electrolysis" effect is formally completed:

$$2F^- \longrightarrow F_2 + 2e$$
 (45)

$$2CF_3 \longrightarrow (CF_3)_2 + 2e. \tag{46}$$

Summary and Conclusions

Throughout this paper the assumption of beam uniformity and stability was maintained. That electron beam stability can be a problem is well known by experimenters in this field. However, it is felt that the paths to ground are the most critical aspect in the work, otherwise the observation of buckling might not have been made. Clearly, the grounding paths and physical effects in the material are in turn related to the charge storage and beam energy thermalization effects. Vaporization is probably related to the proclivity of hydrogen deficient organic materials containing side groups with small steric factors toward sublimation, (this behavior is related to the well known flammability problem). FEP is a highly charge compensated material by virtue of the orientation of its bond dipoles. That these orientations are easily disturbed is evidenced by the well known T⁻¹ dependency. (10) Combined with the charge storage property a temperature effect becomes reasonable.

Examining the buckling effect once more, the dominance of surface storage over bulk storage is suggested, since this distortion moved the surface of the sample closer to the grid or suspended ground as opposed to the bulk ground through the silver to the substrate. Heating combined with charge repulsion can then be used to justify the expansion. Once distorted, charged particle diffusion channels may be formed and the "electrolysis" effect may proceed. The observed browning effect follows as the result of FEP moiety reorientation and "electrolysis".

The electron irradiation of electrical insulators cannot be treated from an experimental approach in a routine manner. A spacecraft passes through space carrying a neutral charge cloud defined with respect to some finite volume, and departure from electrical neutrality

^(9,10) The numbers in parentheses refer to the list of references appended to this paper.

over the surface of this cloud likely exists only as minor electrical fluctuations. Consequently, it appears reasonable to conjecture that for laboratory test data on electron irradiation to be meaningful, data should most probably be obtained using a neutral beam environment. If laboratory simulation of low energy electron and neutral charge distribution fluctuation effects develop into a formidable task, then data from carefully designed spacecraft experiments provide an attractive alternative for two reasons: first, meaningful thermal design data are obtained and second, realistic inputs are obtained for materials development.

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- 10. Debye, P. D., "Polar Molecules", Rheinholt Press, New York, 1929, pp. 27-30.

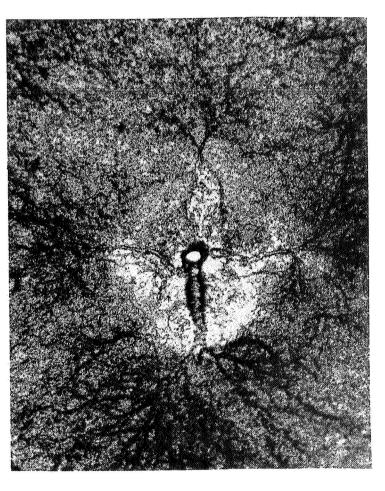
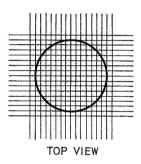


Figure 1. Photomicrograph of FEP Film After Puncture Has Occurred Using 25 Kev Protons at $10^{12} \rm p/cm,^2$ -sec, to $10^{16} \rm p/cm,^2$ (Magnified $100 \times$)



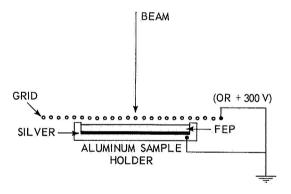


Figure 2. Pictorial Representation Showing Grid Placement Relative to Metalized Sample

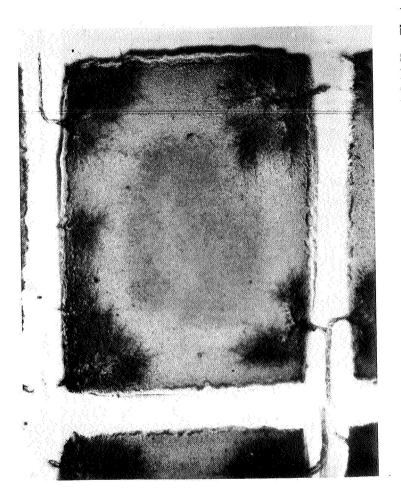


Figure 3. Photomicrograph of Silver Coated FEP Film After Irradiation With 30 Kev Electrons at $10^{12} \rm p/cm$. 2 -sec. to $10^{15} \rm p/cm$. Showing Dendrites (Magnified 50×)

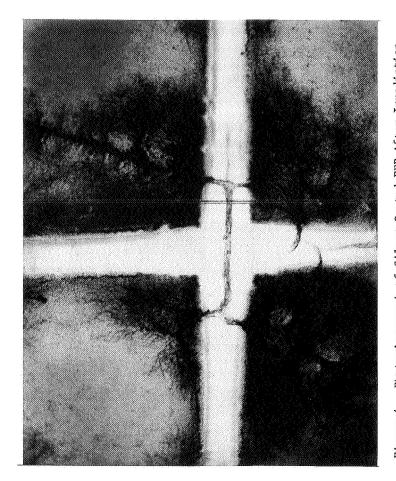


Figure 4. Photomicrograph of Silver Coated FEP After Irradiation With 30 Kev Electrons at $10^{12} \rm p/cm$, 2 - sec. to $10^{15} \rm p/cm$, Showing the Bubbling Effect (Magnified 50X)

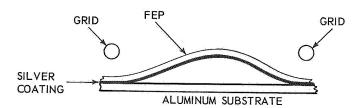


Figure 5. Sectional Representation of Metalized Sample Showing Buckling Position Relative to Two Grid Leads



Figure 6. Photomicrograph of Silver Coated FEP After Irradiation With 30 Kev Electrons at $10^{12} \rm p/cm.^2$ -sec. to $10^{15} \rm p/cm.^2$ Showing Extensive Veining Beneath Charge Shadowed Regions

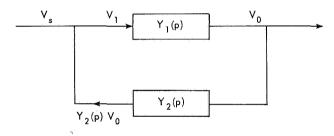


Figure 7. Simple Feed Back Loop Representing Effect of Material Changes on Intrinsic Charge Storage Capability